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Derivatives of Hydrazine. XI. Rotational Isomerism of Methyl Diselenocarbamates and Diselenocarbazates

BRITTA MYNSTER DAHL and PER HALFDAN NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The preparation of methyl diselenocarbamates and diselenocarbazates carrying one or more *N*-alkyl substituents is described. The ^{1}H NMR spectra of these compounds are reported and signals assigned to *Z* and *E* isomers arising from rotational isomerism about the central C–N bond. The assignments are primarily based on multiplicity, position, and solvent shifts of the signals compared with results obtained from analogous compounds with known configuration. The *Z*–*E* isomer ratios are briefly discussed.

During work on derivatives of dithio- and diselenocarbazic acids,[1–4] we became interested in the conformational properties of diselenocarbazic esters. These compounds, in analogy with, *e.g.*, amides [5] and hydrazides,[6,7] may exhibit *Z*–*E* isomerism arising from hindered rotation around the central N^2–C bond. Dipolar structures and selenol forms are also possible in analogy with observations reported for related sulfur compounds.[2,8]

This paper describes a study, primarily by means of ^{1}H NMR spectroscopy, on the rotational isomerism of methyl N^2-methyldiselenocarbazate (*1*), methyl N^2,N^3-dimethyldiselenocarbazate (*2*), and methyl N^2,N^3,N^3-trimethyldiselenocarbazate (*3*) in CCl_4, $CDCl_3$, and nitrobenzene. The compounds prepared for this study, including the three *N*-alkyl-*N*-methyldiselenocarbamates (*4*–*6*) used as reference substances, are listed in Table 1.

The ^{1}H NMR spectra of the compounds *1*–*6* are given in Table 2. The signals arising from the methyl groups (N^2–CH_3, N^3–CH_3, and Se–CH_3) as well as the N^3–H protons can generally be identified by their integrated intensities, multiplicities and relative positions. Furthermore, the signals from the Se–CH_3 groups were characterized by ^{77}Se satellites (J_{Se-C-H} = *ca.* 14 Hz), and in many cases the identity was also established by recording the spectra of the corresponding Se–CD_3 compounds. This procedure was necessary in cases where the chemical shifts of the Se–CH_3 groups were close to those of N^3–CH_3 groups. In the case of *2* the signals from the N^3–CH_3 group collapsed into sharp peaks on addition of D_2O.

With the sole exception of *3* each *N*-methyl group gave rise to two NMR signals when the spectra were recorded at room temperature. Since none of the compounds *1*–*6* carry hydrogen at the N^2 atom, dipolar and selenol forms are not possible. Accordingly the occurrence of two signals from each group must be due to the presence of anisochronous CH_3 groups arising from hindered rotation about the central N^2–C bond. The NMR spectrum of *3* was recorded in a range of solvents and in a temperature range from −55 °C to +140 °C, but it was impossible to detect more than one signal from each group. Since the rotational barrier around the N^2–C bond cannot be much different in the compounds *1*–*3* this is taken as evidence for *3* existing exclusively in one isomeric form.

In order to decide which signals arise from the *Z* form and which from the *E* form, two methods have been used. (1) The chemical shifts of the N^2–CH_3 groups were compared to those of the N^3–CH_3 groups of 3-methyl-1,3,4-selenadiazolidine-2-selones [9] which are necessarily situated in *Z* position. (2) The solvent-induced shifts of the same signals in CCl_4, $CDCl_3$, and $C_6H_5NO_2$ were

Table 1. Preparative data for *N*-alkylsubstituted methyl diselenocarbazates and diselenocarbamates.

Compound	Formula	Method	Yield, %	M.p., °C	Analyses (C, H, N)
1 $NH_2-N(CH_3)-CSeSeCH_3$	$C_3H_8N_2Se_2$	A	79	134–135	Calc.: 15.66; 3,52; 12.18 Found: 15.44; 3.45; 12.14
2 $CH_3NH-N(CH_3)-CSeSeCH_3$	$C_4H_{10}N_2Se_2$	B	80	65.0–66.5	Calc.: 19.68; 4.13; 11.48 Found: 19.66; 4.20; 11.58
3 $(CH_3)_2N-N(CH_3)-CSeSeCH_3$	$C_5H_{12}N_2Se_2$	B	85	55–57	Calc.: 23.27; 4.69; 10.85 Found: 23.12; 4.72; 11.00
4 $(CH_3)_2N-CSeSeCH_3$	$C_4H_9NSe_2$	C	72	84–85	Calc.: 20.97; 3.96; 6.12 Found: 20.70; 3.86; 6.10
5 $(C_2H_5)(CH_3)N-CSeSeCH_3$	$C_5H_{11}NSe_2$	D	30	5.5–7.0	Calc.: 24.71; 4.56; 5.76 Found: 24.40; 4.53; 5.92
6 $(i\text{-}C_3H_7)(CH_3)N-CSeSeCH_3$	$C_6H_{13}NSe_2$	D	50	[a]	Calc.: 28.03; 5.10; 5.45 Found: 28.10; 5.16; 5.47

[a] Melted during drying at 0 °C.

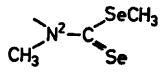
compared. The previously obtained data for 3-methyl-1,3,4-selenadiazolidine-2-selones [9] were supplemented as shown in Table 3. It is seen, that (1) the $CH_3-N-CSe$ signal of the *Z* form shows a chemical shift in $CDCl_3$ between 3.50 and 3.64 ppm, and (2) it is displaced towards lower δ-values when the compounds are recorded in CCl_4 solution, but towards higher δ-values in $C_6H_5NO_2$.

From the results listed in Table 2 it is seen, that the low-field N^2-CH_3 signals have chemical shift values in $CDCl_3$ in the range 3.48–3.88 ppm while the high-field signals are located in the range from 3.17 to 3.55 ppm. Though this indicates that it is the former signals which should be assigned to the *Z* CH_3 group there is a certain overlap of the regions and a confirmation is clearly needed for this assignment.

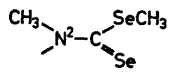
Considering next the solvent shifts, it is seen that the low-field N^2-CH_3 signals behave uniformly and differently from the high-field N^2-CH_3 signals. Thus, the low-field N^2-CH_3 signals ($CDCl_3$) are shifted to lower field in nitrobenzene and to higher field in CCl_4. The high-field N^2-CH_3 signals are found at almost identical positions in CCl_4 and $CDCl_3$, but are shifted to higher field in nitrobenzene solution. This result is only compatible with an assignment of the low-field N^2-CH_3 signals to the CH_3 group in *Z* position.

The *Z*–*E* isomer ratios for the diselenocarbamates *5* and *6* are both close to 1:1. This indicates that the steric requirements of =Se and $-SeCH_3$ are not significantly different for the compounds studied, that is provided the size of a substituent on the N^2-atom does not exceed that of an isopropyl group. In the case of the diselenocarbazates *1*–*3* there seems to be a definite tendency for predominance of the *Z* form. Walter and Reubke [7] has explained the predominance of the *E*-form in hydrazides (corresponding to the present *Z*-forms) with substituents exerting no steric influence to the tendency towards intramolecular compensation of existing dipoles. Since the diselenocarbazates *1*–*3* undoubtedly exhibit significant bond moments along the C=Se and N–N bonds, the predominance of the *Z* forms can be explained in an analogous way by the mutual repulsion of these dipoles.

Table 2. ^{1}H NMR chemical shifts (δ, ppm) at *ca.* 40 °C of *N*-alkylsubstituted methyl diselenocarbazates and diselenocarbamates. Abbreviations: s = singlet, d = doublet, q = quartet, and sep = septet. Centers of multiplets are given.



Z-isomer

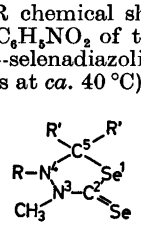


E-isomer

Compound	*Z*, %			N^2-CH_3			N^3-CH_3	$Se-CH_3$
	CCl_4	$CDCl_3$	$C_6H_5NO_2$	CCl_4	$CDCl_3$	$C_6H_5NO_2$	$CDCl_3$	$CDCl_3$
Z-isomer								
1[f]		50	80		3.88s	4.00s		2.47s
2[g]	75	75	90	3.67s	3.73s	3.83s	2.75d[a,b]	2.40s[c]
3	100	100	100	3.42s	3.48s	3.55s	2.63s	2.40s
4	(50)	(50)	(50)	3.60s	3.68s	3.62s		2.63s
5[d]	50	50	50	3.55s	3.60s	3.60s		2.65s
6[e]	45	45	45	3.41s	3.48s	3.52s		2.67s
E-isomer								
1[f]					3.55s	3.50s		2.70s
2[g]				3.42s	3.43s	3.37s	2.70d[a,b]	2.65s[c]
3								
4				3.40s	3.38s	3.27s		2.63s
5[d]				3.33s	3.32s	3.25s		2.65s
6[e]				3.16s	3.17s	3.16s		2.67s

[a] On addition of D_2O the signal collapsed to a sharp peak. [b] J_{NH-C-H} is approximately 6 Hz. [c] The signal was absent in the spectrum of the corresponding $Se-CD_3$ esters. [d] The signals from the ethyl group are: CH_3, broad triplet with center at 1.32. CH_2 (*Z*) 3.84 q, CH_2 (*E*) 4.29q. J_{CH-C-H} = *ca.* 7 Hz. [e] The signals from the isorpopyl group are: CH (*Z*) 4.79sep, CH_3 (*Z*) 1.33d, CH (*E*) 6.20sep, CH_3 (*E*) 1.27d J_{CH-C-H} = *ca.* 7 Hz. [f] NH_2 *ca.* 4.7 ($CDCl_3$), *ca.* 4.8 ($C_6H_5NO_2$). [g] Only N^3-H (*Z*) was identified with certainty: *ca.* 4.1 (CCl_4), *ca.* 4.2 ($CDCl_3$), *ca.* 4.8 ($C_6H_5NO_2$).

Table 3. ^{1}H NMR chemical shifts (δ, ppm) in CCl_4, $CDCl_3$ and $C_6H_5NO_2$ of the N^3-CH_3 group in 3-methyl-1,3,4-selenadiazolidine-2-selones. (*Ca.* 3 % solutions at *ca.* 40 °C).



Compound	CCl_4	$CDCl_3$	$C_6H_5NO_2$
R = R′ = H		3.60	3.68
R = H, R′ = CH_3[g]	3.62	3.64	3.73
R = CH_3, R′ = H	3.47	3.50	3.53
R = R′ = CH_3[g]	3.50	3.55	3.59

EXPERIMENTAL

The analyses were carried out in the microanalysis department of this laboratory. Melting points were determined in capillary tubes and were not corrected. Infrared spectra were obtained on a Perkin-Elmer model 337 grating infrared spectrophotometer and the proton magnetic resonance spectra on a Varian A-60 A instrument with tetramethylsilane as an internal standard.

The directions given below for the preparations of the methyl esters refer to the entry "Method" in Table 1.

Salts used as starting materials for the preparation of esters:

Dialkylammonium 2,2-dialkyldiselenocarbamates. One ml of 10 M aqueous sodium hydroxide was added to a suspension of the amine hydrochloride (10^{-2} mol) in pentane (100 ml) cooled in an ice bath. The mixture was shaken

vigorously and dried (KOH). Into the stirred solution of the liberated amine at 0°C a solution of carbon diselenide (5×10^{-3} mol) in pentane (40 ml) was added dropwise over a period of 2 h in a nitrogen atmosphere. The yellow solid that separated was collected on a glass filter, washed with pentane and dried *in vacuo*.

Hydrazinium diselenocarbazates. Generally, these salts were prepared analogously to the diselenocarbamates described above, starting with the free hydrazines and using dry ether as the solvent.[10]

Method A. Methyl iodide (10^{-3} mol) was added to a filtered, aqueous solution (4 ml) of the appropriate hydrazinium salt (10^{-3} mol). The reaction mixture was stirred vigorously at room temperature until it was (nearly) colourless. The crystals that precipitated were collected by centrifugation, washed with a small amount of cold water and dried *in vacuo*.

Method B. An ethanolic solution (4 ml) of methyl iodide (10^{-3} mol) was added to a filtered aqueous solution (5 ml) of the appropriate hydrazinium salt (10^{-3} mol). The reaction mixture was stirred for 5 – 10 min at room temperature and the solvent was evaporated *in vacuo* with gentle heating until a volume of ½ – 1 ml was reached. This residue was extracted with pentane and the pentane solution dried ($MgSO_4$) and taken to dryness. The residue (R) of yellow to colourless crystals was washed with a small amount of cold pentane.

Method C. An aqueous solution (5 ml) of dimethylammonium 2,2-dimethyldiselenocarbamate (2×10^{-3} mol) was added to an ethanolic solution (3 ml) of methyl iodide (2×10^{-3} mol) with stirring. More water (10 ml) was added to ensure complete precipitation. The light yellow crystalline compound was washed with water and dried *in vacuo*.

Method D. As Method B. The residue (R) consisted of an oil, which was purified by dissolution in the minimum amount of pentane and cooling to *ca.* −80 °C with scratching. The solid that separated, which in all cases melted below room temperature, was quickly collected by centrifugration, washed with a small amount of cold pentane and dried *in vacuo*.

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